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VAPOR PHASE IMPREGNATION OF ACTIVE CARBONS

FINAL SUMMARY

(January 3, 1969 - April 3, 1970)

by

D. Marshall Andrews

April 1970



DEPARTMENT OF THE ARMY  
EDGEWOOD ARSENAL  
Physical Research Laboratory  
Edgewood Arsenal, Maryland 21010

Contract DAAA15-69-C-0302  
Project 1B662706A095

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## FOREWORD

The work described in this report was authorized under Project 1B662706A095, CB Physical Protection Investigations (u). This report covers work completed in the period January 3, 1969 to April 3, 1970.

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The author wishes to thank Mr. D. Frank Bazzarre of Commonwealth Scientific Corporation for his assistance in the management of this program and Dr. John P. Redmond for his technical guidance. Special thanks to Mr. Leonard Jonas, Contract Project Officer, Physical Research Laboratory, Edgewood Arsenal, Edgewood Arsenal, Maryland, for his many helpful suggestions and observations; Mr. Al Oglesby, Physical Research Laboratory, Edgewood Arsenal, Edgewood Arsenal, Maryland, who performed most of the toxic agent breakthrough tests; Dr. Frank Vastola, Mineral Science Building, Pennsylvania State University, Department of Fuel Science, University Park, Pennsylvania, who supervised the sample testing and supplied technical assistance.

### SUMMARY

This report summarizes the accomplishments of a 13 month program to study vapor impregnation processes as a means for producing carbons having increased protection against toxic agents. Processes were developed for the vapor impregnation of carbon with cupric oxide, chromium trioxide, aluminum chloride and platinum.

Spectrographic analysis of impregnated samples indicated that impregnants were present on these carbons in the expected concentration range. BET surface area analysis proved that material deposited by vapor impregnation processes caused less loss of surface area than equal amounts of material deposited by conventional solution processes. Pore size distribution calculations revealed that vapor impregnation processes deposited material in all carbon pores, while solution processes deposit material only in pores larger than 12 Å in diameter.

Copper-chromium (oxide) vapor impregnated carbons were subjected to treatments designed to produce an impregnant with CK activity similar to a solution impregnated ASC carbon. Samples were produced which had greater CK activity than an unimpregnated carbon, but less activity than an ASC carbon. Future work plans designed to optimize the vapor deposition and treatment of copper-chromium oxides, to produce carbon with several times the CK capacity of an ASC, are reviewed.

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## VAPOR PHASE IMPREGNATION OF ACTIVE CARBONS

### 1.0 INTRODUCTION

There is a continuing need for improving activated carbons' capability to remove toxic gases. Since this capability is due primarily to adsorption on the carbon surface, the amount of toxic material removed is determined by the amount of surface area of the carbon and the affinity of the carbon for the particular toxic agent. Furthermore, the agent is not chemically altered by the carbon, and desorption results in recontamination of the air by the toxic compound.

The degree of increased adsorption capacity which can be achieved by enlarging surface area through greater activation has practical limits. Therefore, further increases in capacity must come from methods which increase carbons' affinity for the particular agent. One such method consists of impregnating an active carbon with a metal or metal salt capable of reacting with the particular toxic agent. Ideally, the impregnant should catalytically decompose or alter the toxic species to form a nontoxic compound. Then, provided that the catalyst impregnant is not poisoned, the impregnated carbon would offer protection indefinitely. Many fold increases in protection can be achieved by impregnations with compounds which chemically react to decompose or combine with toxic species.

Generally, the impregnation of active carbons is achieved by a solution process in which a suitable carbon is soaked in a solvent, usually water, containing the impregnant. Subsequent drying of the carbon then results in precipitation of the impregnant on the carbon surface. This procedure has several drawbacks. For example, since a solvent is used, the impregnant cannot penetrate into pores smaller than the solvated molecule. This results in an uneven distribution of impregnant, with none being deposited in the small carbon pores. An activated carbon, with a large macropore area and consequently, a relatively small overall area, must be used in order to get an effective distribution of impregnant. Furthermore, since deposition occurs by precipitation, the material tends to form in nodules rather than as a thin, even coating.

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This program is directed at investigating vapor phase deposition processes as a means to more effectively impregnate carbons. This method consists of allowing a gas, composed of a compound capable of being condensed or decomposed into the desired impregnant, to permeate throughout the carbon. The gas is then condensed or decomposed to deposit the impregnant. Since no solvent is involved, the impregnant should be able to enter the smaller carbon pores. Furthermore, the atom by atom fashion in which vapor deposition occurs results in a thin, even, highly active film of impregnant.

## 2.0 APPROACH

Four materials were chosen as candidates for study by vapor impregnation methods. The first two, copper and chrome, were to be deposited on the same carbon in an attempt to produce an impregnant with activity against CK (cyanogen chloride) greater than that shown by solution impregnated AC whetlerite. The third material, aluminum chloride was chosen as a study of vapor impregnation with a metal halide. The fourth candidate material was platinum, deposited as the metal in an attempt to produce an impregnated carbon having activity approaching that of a homogeneous catalytic system.

Processes were selected for investigation which tended to deposit the candidate materials either in the form necessary to produce activity, or in a form which could easily be converted to the active species. The actual chemical form of the catalyst present on an AC whetlerite is unknown. However, previous work at Edgewood Arsenal revealed that copper must be present as the +2 oxide, and chromium as the +6 oxide. Consequently, the metal organic copper acetylacetonate (CuAA) was chosen for the deposition of copper. This material is a solid melting at 230°C and decomposing above 240°C to yield copper metal and acetylacetone. Subsequent treatments with oxidizers were used to convert the deposited copper metal to the necessary +2 oxide. Three methods were investigated for the deposition of chromium. The metal can be deposited by pyrolysis of the vapors of the metal organic dicumene chromium (DCCr) a dark green liquid which decomposes above 300°C. Treatment with strong oxidizers was then necessary to produce the +6 oxide. For the second method, chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ) was vaporized under vacuum and adsorbed on the carbon. Controlled hydrolysis then produces the +6 oxide according to the reaction,  $\text{CrO}_2\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{CrO}_3 + 2\text{HCl}$ . The final method investigated was the direct sublimation of  $\text{CrO}_3$  into the carbon pores.

Aluminum chloride impregnation was accomplished by direct vacuum sublimation of the halide into the carbon pores. At atmospheric pressure, aluminum chloride sublimes at 177.8°C. Platinum was deposited as the metal, so the metal organic platinum acetylacetonate

(PtAA) was utilized for platinum impregnations. PtAA is a yellow solid that can be sublimed in vacuum at  $180^{\circ}\text{C}$  and decomposes at  $350^{\circ}\text{C}$  to yield platinum metal and acetylacetone.

Samples prepared using these procedures were subjected to three tests to determine their respective properties. These tests include the following:

- 1) Analytical tests; such as simple qualitative tests were performed to determine the presence of the impregnant on the carbon, and the oxidation status of the catalyst. Semiquantitative spectrographic analysis were used to determine the amount of catalyst present, and X-ray diffraction studies were performed in an attempt to identify the molecular composition of the catalyst.
- 2) Surface area tests were performed to determine changes in the physical properties of the carbon caused by impregnation. The standard BET nitrogen adsorption isotherm data plot<sup>(4)</sup> was utilized to detect changes in total surface area. Calculations of pore-size distribution were made from these data using the procedure devised by Cranston<sup>(5)</sup> and comparison of these distributions aided in determining coating distribution and penetration. Photomicrographs of the carbon surface utilizing the scanning electron microscope were studied in an attempt to observe changes in the surface caused by impregnation.
- 3) Detoxification tests were performed on samples of vapor impregnated carbons to determine increases in activity resulting from impregnation. Copper-chromium impregnated carbons were tested at Edgewood Arsenal against CK and compared to type AC solution impregnated carbons. Evaluation with PS ( $\text{CCl}_3\text{NO}_2$ ) indicated changes in adsorption capacity of the carbon due to surface area reduction caused by impregnation. An HCl breakthrough test was devised, and copper impregnated carbons were tested at Commonwealth Scientific to determine post-impregnation treatments which produced the most active copper.

### 3.0 EXPERIMENTAL PROCEDURE

#### 3.1 Copper Impregnation

Several difficulties appeared in the first copper impregnation runs using copper acetylacetonate (CuAA). The metal organic was sublimed from a vaporizer about 4 in away from the carbon to be impregnated, and large amounts of the material condensed out on the deposition chamber walls without reaching the carbon. The small difference between sublimation temperature and decomposition temperature of CuAA resulted in much of the compound decomposing in the vaporizer. These experiments, however, did show that carbon has a strong affinity for CuAA, since the small amount which did reach the carbon was readily adsorbed.

In order to take advantage of this affinity, it was decided to dry mix the carbon and the copper acetylacetonate and heat the mixture under vacuum. This procedure minimized the distance a molecule of CuAA vapor must travel before contacting the carbon, and thus reduced the possibility of its decomposing or condensing elsewhere.

The first runs using this procedure proved to be successful. At a temperature of 70°C and a pressure of 150 $\mu$ , all the CuAA had been adsorbed into the carbon as evidenced by the disappearance of the blue colored CuAA. Decomposition of the organo-metallic begins at a carbon temperature of about 100°C with a pressure of 150 $\mu$ . The rate of decomposition continues to increase without loss of reactant up to 200°C and 350 $\mu$ . Under these conditions, the occurrence of CuAA sublimation is evidenced by condensation of material on the cool neck of the reaction flask.

Several runs made using this method, resulted in the following procedure for vapor impregnating carbon with copper from CuAA.

##### I Outgas Carbon

- (a) Weigh into a round bottom flask of known tare, the quantity of carbon to be impregnated (not to exceed 1/2 the flask volume).

- (b) Connect the flask to the vacuum system [Fig. 1] and begin evacuating.
- (c) Turn on oil bath. Heat and set control for 300°C.
- (d) Keep a record of temperature and pressure variations.
- (e) When pressure is less than 250 $\mu$  for a carbon temperature of 300°C, turn off heat.
- (f) When carbon temperature drops below 150°C, return system to atmospheric pressure.
- (g) Reweigh carbon and determine weight loss.

## II Impregnate Carbon

- (a) To the flask containing the carbon from Part I, add the amount of CuAA to give the desired weight percent of copper [CuAA is 24.3% Cu by weight, therefore, it requires four times the weight of CuAA to obtain a given weight percent Cu; i.e., for a 100-gm sample of carbon add 16-gm CuAA to get a 4% by wt copper impregnation]
- (b) Shake the flask to intimately mix the carbon and CuAA.
- (c) Connect flask to vacuum system Fig. 1 and begin pump down.
- (d) When pressure drops below 500 $\mu$ , turn on heat and set for 100°C.
- (e) Keep a record to temperature and pressure variations.
- (f) After carbon has reached 100°C and all of the CuAA has been adsorbed, set temperature for 180°C.
- (g) Keep carbon temperature between 180° and 190°C until pressure drops, indicating decomposition is almost complete; then set temperature for 275°C to complete the reaction.

- (h) When pressure begins to drop at  $275^{\circ}\text{C}$ , turn off heat and allow carbon to cool down below  $100^{\circ}\text{C}$ .
- (i) Restore system to atmospheric pressure and weigh carbon.

From the initial carbon weight, final carbon weight and weight of CuAA used, the efficiency of the decomposition reaction can be calculated. If the above procedures are followed, the reaction will be better than 90% complete, and very little CuAA will be lost through sublimation. Because the rate of decomposition is rather slow below  $200^{\circ}\text{C}$ , this procedure requires a relatively long reaction time. A 150 gm sample of carbon to be impregnated with 4% by weight copper requires about 7 hr utilizing this method. Time requirements can be reduced considerably by ignoring Step 2 and raising the temperature up to  $275^{\circ}\text{C}$ ; however, as much as 20% of the CuAA will be lost through sublimation.

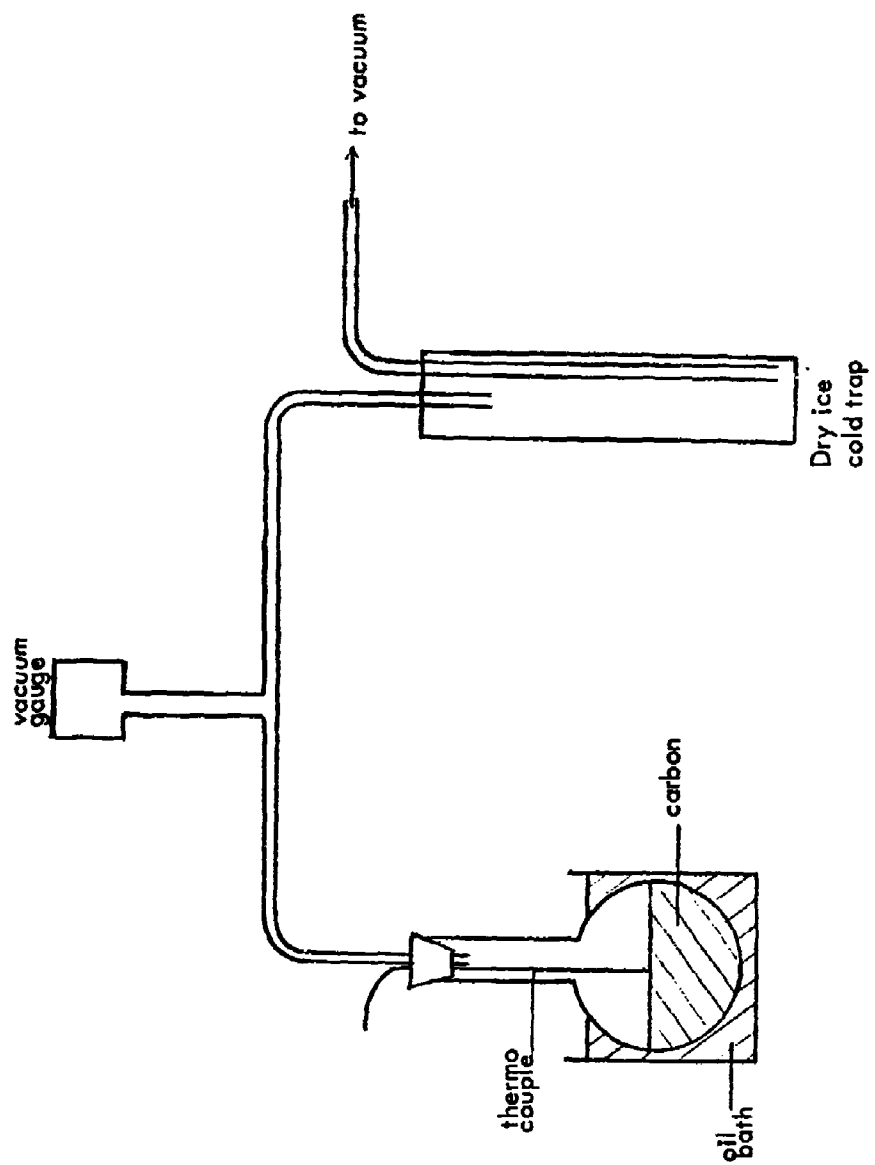
### 3.2 Chromium Impregnation

As a result of difficulties involved in oxidizing chromium from the metal to the +6 state (necessary for CK activity) it was decided to postpone examination of deposition processes involving dicumene chromium in favor of the more direct chromyl chloride vaporization and chromium trioxide sublimation methods. Even with chromyl chloride, a hydrolysis step is necessary to produce the +6 oxide, thus initial experiments were performed using chromium trioxide.

Experience with copper impregnation from CuAA has established that materials with low vapor pressure such as chromium trioxide must be brought in close initial contact if vapor impregnation is to be achieved. As a result, dry chromium trioxide was mixed with out-gassed carbon in the same manner as CuAA for copper impregnation, (See Fig. 1) a vacuum drawn, and the material heated. Several runs were made using this method with each run having a different ultimate sublimation temperature. Analysis of the carbon after each run revealed that in all cases little or no chromium trioxide had been adsorbed by the carbon. Pressure rises noticed above  $150^{\circ}\text{C}$  during impregnation



FIGURE 1



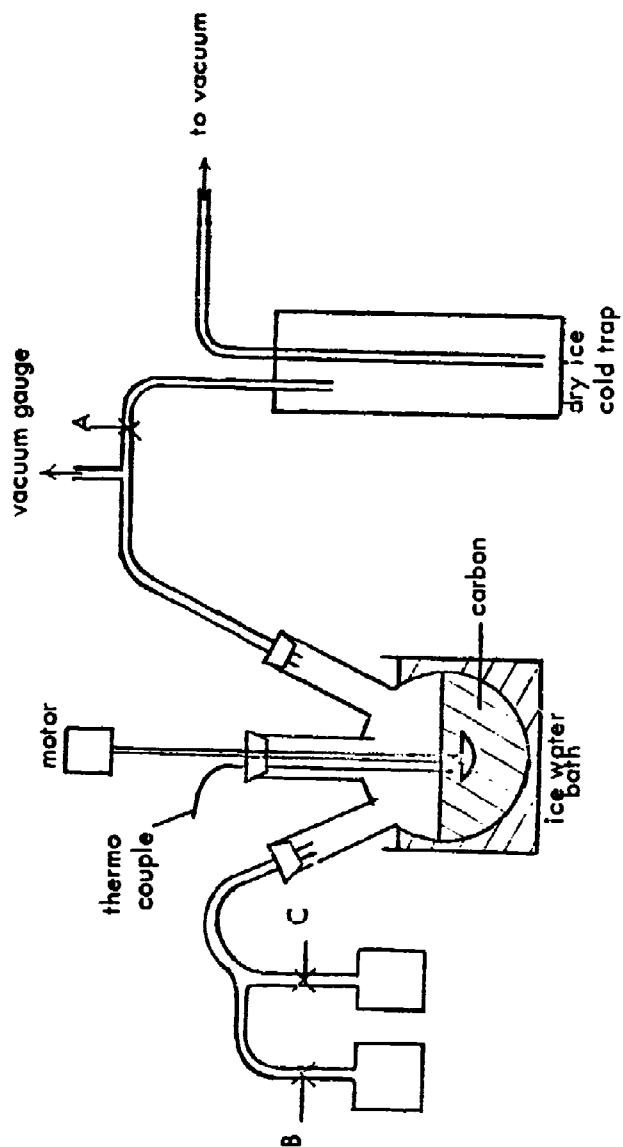
COPPER IMPREGNATION APPARATUS

indicated also that reduction of the chromium trioxide which did adsorb on the carbon was occurring, with the production of some gaseous species, probably carbon dioxide. These results revealed that chromium trioxide unlike CuAA, has little or no tendency to adsorb on carbon. Carbon samples were impregnated with ammonia and water in an attempt to increase the affinity of carbon for chromium trioxide. Samples from this run tested for chromium trioxide showed that very little of the oxide had been adsorbed. This, combined with the low vapor pressure of chromium trioxide and its ease of reduction to chromic oxide at elevated temperatures, ruled out vacuum sublimation as a method of vapor impregnating carbon with chromium trioxide.

The next method involved the use of chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , a dark red liquid, which boils at  $117^\circ\text{C}$ . This material may be converted to chromium trioxide by water or any other compound capable of replacing the chlorine in chromyl chloride with oxygen. The first experiment with chromyl chloride consisted of vaporizing the material under vacuum into copper impregnated carbon placed in a glass tube. This test showed that carbon has a strong affinity for chromyl chloride as a large amount of the compound was adsorbed by the carbon, and heat was generated during the adsorption. Having saturated the carbon with chromyl chloride, water vapor was introduced in order to hydrolyze the chromyl chloride to chromium trioxide. Once again heat was generated. Analytical tests performed on the material from this experiment indicated that some of the chromium had been reduced to the +3 state, and some of the copper had been converted to cupric chloride.

In order to prevent the conversion of cupric oxide to cupric chloride, ammonium hydroxide was investigated as a means to tying up the chlorine. Runs made by this ammonolysis treatment also yielded heat and revealed some reduction of chromium to the +3 state, however, no cupric chloride was detected. Finally, an ice bath was used to keep the heat generated during the reaction from becoming excessive. Tests made on samples from this run indicated no reduction of +6 chromium and no formation of cupric chloride. These results led to the construction of the chromyl chloride vapor impregnation apparatus shown in Fig. 2. Further impregnation runs were made at  $-70^\circ\text{C}$  by immersing the reaction flask in a Dry Ice acetone bath in an effort to reduce the

FIGURE 11



CHROMIUM IMPREGNATION APPARATUS

reactivity of chromyl chloride. Under these conditions, it was possible to impregnate the carbon in the absence of ammonia without the formation of cupric chloride or the reduction of Cr<sup>+6</sup> to Cr<sup>+3</sup>. This led to the adoption of the following method for the vapor deposition of chromium trioxide from chromyl chloride:

- (a) Place previously copper impregnated carbon into flask shown in Fig. 2 and evacuate.
- (b) When pressure drops below 500 $\mu$ , immerse the reaction flask in a dry ice-acetone bath.
- (c) When carbon temperature drops below -70°C, turn on stirrer, close valve A and open valve C, and allow a measured amount of chromyl chloride to vaporize into the carbon.
- (d) When impregnation is complete, close valve C and open valve A.
- (e) When pressure drops below 200 $\mu$ , remove flask from the dry ice-acetone bath and raise carbon to room temperature, allowing chromyl chloride to distribute itself evenly throughout the carbon.
- (f) When pressure again drops to 200 $\mu$ , place flask back in dry ice-acetone bath and cool carbon down to -70°C.
- (g) When carbon has been cooled down, close valve A and open valve B to allow water, ammonium hydroxide or other catalyst to enter.
- (h) When hydrolysis is complete, warm carbon to room temperature, and restore to atmospheric pressure.

This procedure deposits chromium as the +6 oxide, which is the form necessary for activity against toxic agents. Activity also depends on the deposition of copper and chromium within molecular distances of each other, and the great differences in the physical and chemical properties between a molecule of CuAA and a molecule of chromyl chloride may

cause the two materials to be deposited on different areas of the carbon particle. Thus it was felt that an investigation of impregnation using DCCr, an organic compound more like CuAA, would be worthwhile.

The chromium impregnations using DCCr, a dark green liquid at room temperature, were performed in the same apparatus, by the same procedure as was used for impregnations with copper. Because of the air and moisture instability of DCCr, the liquid was transferred onto dry, out-gassed carbon in a nitrogen atmosphere. A vacuum of about 500 $\mu$  was drawn on the carbon and heat applied by an oil bath.

Carbon showed the same affinity for DCCr that it had shown for CuAA. At a temperature of about 90°C, all of the DCCr had been adsorbed. Decomposition of the reactant began at 150°C and was complete at 350°C. Very little of the DCCr was lost through vaporization from the reaction flask.

Tests on carbon impregnated from DCCr showed that chromium was present as the metal, and would have to be oxidized to the +6 state. One sample was prepared and sent to Edgewood Arsenal in the as-plated condition where it was tested for toxic agent removal capabilities. The other samples were treated in various ways in an effort to oxidize the chromium, and tested for the presence of Cr+6.

Treating samples of plain carbon and copper impregnated carbons with water and ammonia in air at atmospheric pressure failed to oxidize the chromium in either sample. Saturating the samples of plain carbon and copper impregnated carbon with ammonia and water and placing them under 100 psi carbon dioxide pressure at 80°C also failed to oxidize the chromium. Finally, a sample of Cu-Cr impregnated carbon was boiled in 30% hydrogen peroxide solution and heated to 150°C to dry. Another sample of the same material was placed under oxygen pressure of 40 psi for 24 hr and then dried at 150°C. Neither of these samples indicated appreciable oxidation of the chromium and as a result, no further work with DCCr was warranted.

### 3.3 Aluminum Chloride Impregnation

This section of the program called for the vapor deposition of a metal chloride onto active carbon. The metal chloride to be investigated was aluminum chloride which cannot be deposited from aqueous solution because of the reaction  $\text{AlCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{Al}(\text{OH})_3 + 3\text{HCl}$ .<sup>(6)</sup> Upon evaporation of the water, the oxide or hydroxide of aluminum is obtained.

Aluminum chloride is a white solid at room temperature and sublimates at  $178^\circ\text{C}$ . The first impregnation procedure used was designed to take advantage of this low sublimation temperature by directly vaporizing the material into the carbon under vacuum. Because of the reaction previously indicated, extra care must be taken to exclude as much water as possible from the carbon and impregnation apparatus.

The procedure used in the preparation of a 5% by weight aluminum chloride vapor impregnated carbon is as follows:

- 1) Weigh carbon sample
- 2) Place in reaction flask and connect to impregnation apparatus. (Same system as used for copper impregnation.)
- 3) Turn on vacuum and set heat control for  $400^\circ\text{C}$ .
- 4) Hold carbon at  $400^\circ\text{C}$  for three hours.
- 5) Cool system to room temperature and back fill with dry nitrogen.

#### Impregnation

- 1) Weigh, in a dry atmosphere, the amount of aluminum chloride necessary to make a 5% by weight impregnation.
- 2) Transfer the aluminum chloride to the impregnation flask and mix with the carbon.
- 3) Evacuate the impregnation flask to about  $200\mu$  pressure.
- 4) Set temperature controls for  $200^\circ\text{C}$ .
- 5) Maintain temperature at  $200^\circ\text{C}$  until all of the aluminum chloride has been adsorbed (approximately

- 1/2 hr).
- 6) Cool system to room temperature and back fill with dry nitrogen.

A sample of carbon impregnated with aluminum chloride by the above procedure was sealed with wax to prevent adsorption of moisture, and sent to Edgewood Arsenal for testing.

### 3.4 Platinum Impregnation

This phase of the program calls for the vapor deposition of platinum, as the metal, onto activated carbon. The results achieved with the deposition of copper from the acetylacetonate led to the search for a similar compound containing platinum. Platinum acetylacetonate (PtAA) was chosen for initial deposition studies. This compound is a light yellow powder which can be sublimed in vacuum at 180°C, and decomposes at 350°C to yield platinum metal and acetylacetone.

The same system and procedure outlined previously for use with copper was used for the deposition of platinum. Adsorption of PtAA by carbon took place at 75°C at a pressure of 240μ. Decomposition began at 190°C but was rather slow up to 250°C. A temperature of 325°C was necessary to complete the decomposition.

Three weight percentages of platinum 0.5%, 1% and 5% were prepared using this method. Two additional samples were further activated by treatment with hydrogen at elevated temperatures. This was accomplished by placing a sample of Pt impregnated carbon in the impregnation apparatus, evacuating and heating the carbon to 300°C. When temperature was reached, the flask was back filled with hydrogen and returned to room temperature; two samples, 0.5% and 5% by weight impregnation, were treated. Samples of each weight percent impregnation were forwarded to Edgewood Arsenal for testing.

These results are reported in Appendix III.

## 4.0 EXPERIMENTAL RESULTS

### 4.1 Analytical Tests

#### 4.1.1 Qualitative Tests

Simple chemical qualitative analysis tests were used to determine the presence of copper and chromium trioxide on carbon following impregnation. These were conducted in the following manner:

- a) The impregnated carbon is soaked in twice its volume of 28%  $\text{NH}_4\text{OH}$  solution, with stirring, for 15 min.
- b) The solution is then filtered and lead acetate added to the decant. The appearance of a yellow precipitate of lead chromate indicates the presence of chromium trioxide.<sup>(7)</sup>
- c) An excess of lead acetate is added and the solution is again filtered.
- d) The appearance of a bright blue color (tetramine copper complex) in the filtered solution indicates the presence of copper.<sup>(8)</sup>

Results of these tests indicated that the procedure for the deposition of copper from CuAA produced a coating of copper on all of the carbon particles and that the chromyl chloride procedure deposited chrome as chromium trioxide.

#### 4.1.2 Spectrographic Analysis

The actual amount of impregnant present on the carbon was determined by semiquantitative spectrographic analysis. Spectrographic analysis was conducted on samples of plain carbon, 8% by weight copper vapor impregnated carbon, 8% copper -3% chromium trioxide vapor impregnated carbon, 5% platinum vapor impregnated carbon, and type ASC liquid impregnated carbon. The results of these analysis can be seen in Table I.



TABLE I

## SPECTROGRAPHIC ANALYSIS OF CARBON SAMPLES

CONCENTRATION  
(PERCENT BY WEIGHT)

ELEMENT	PLAIN CARBON	8% Cu	8% Cu 3% CrO <sub>3</sub>	ASC	5% Pt
Pt	--	--	--	--	4.1
Cu	0.005	7.0	7.0	3.5	0.005
Cr	0.004	0.004	2.0	0.7	0.004
Ag	--	--	--	0.05	--
B	0.004	0.004	0.004	0.004	0.004
Mn	0.005	0.008	0.005	0.005	0.005
Mg	0.04	0.04	0.04	0.04	0.04
Ca	0.03	0.03	0.03	0.03	0.03
Be	0.0003	0.0003	0.0003	0.0003	0.0003
Ti	0.03	0.04	0.03	0.03	0.03
Al	0.7	0.7	0.7	0.7	0.7
Na	0.4	0.4	0.4	0.4	0.4
Y	0.003	0.003	0.003	0.003	0.003
Zr	0.004	0.004	0.004	0.004	0.004
Ni	0.008	0.009	0.008	0.008	0.008
Co	0.004	0.004	0.004	0.004	0.004
Sr	0.03	0.03	0.03	0.03	0.03
Ba	0.02	0.02	0.02	0.02	0.02
V	0.01	0.01	0.01	0.01	0.01
Fe	0.2	0.2	0.2	0.2	0.2
Sc	0.002	0.002	0.002	0.002	0.002
Si	0.7	0.7	0.7	0.7	0.7

The concentration of impregnants on the vapor deposited samples are within the expected range. The solution impregnated ASC, however, contains only one-half the expected concentration of impregnants. A whetlerite solution contains approximately 8% copper and 3% chromium trioxide, but the impregnated carbon contains 3.5% copper and 0.7% chromium (or 1.4% chromium trioxide). These results show that vapor impregnated carbons are more efficiently prepared, since less impregnant is lost in processing. Furthermore, a tighter control of impregnant concentrations can be maintained with vapor impregnation methods. Attempts to identify the molecular structure of the deposit produced on an ASC and Cu-Cr vapor impregnated carbon, using X-ray diffraction methods were unsuccessful. The samples produced only fogs even after 24 hr exposure, indicating that the coating on both samples are in a thinly divided, amorphous condition.

#### 4.2 Surface Area Tests

##### 4.2.1 Nitrogen Adsorption Isotherm

Total surface area determinations from nitrogen adsorption isotherms using the standard BET datum plot were prepared for four samples of impregnated carbons, and one sample of untreated PCC grade CWS carbon. These results can be seen in Table II. All of the impregnated samples showed a decrease in surface area, with the exception of the platinum impregnated, which had a 10% increase in surface area. The platinum sample was prepared and tested at a different time than the other samples, this could account for the variation. It is obvious from these results, however, that the vapor impregnation of carbon with platinum at this concentration does not have a damaging effect on the carbon surface area.

A comparison of the surface area loss for the copper-chromium vapor impregnated carbon and the copper-chromium ASC solution impregnated carbon revealed that both samples lost approximately the same amount of surface area, although previous spectrographic analysis had shown

that the vapor impregnated sample had twice as much material on it. This could be due to a more even coating produced by vapor impregnation techniques, which tends to deposit the material as a thin coating on the inside of the carbon pores. Solution impregnation processes, which deposit material by evaporating away water trapped in the carbon pores and crystallizing out the impregnants, may tend to plug pores and deposit material in nodular form which would considerably reduce surface area.

TABLE II  
BET SURFACE AREA

Sample	Surface Area (mm <sup>2</sup> /gm)	% Drop
Plain	1125	0.0
8% Cu	952	15.4
8% Cu-3% CrO <sub>3</sub>	764	32.0
ASC	788	30.0
5% Pt.	1246	--

#### 4.2.2 Pore Size Distribution

Pore size distribution calculations were made on the carbon samples using the Cranston method. Since these calculations are long and involved, a computer program was written at Edgewood Arsenal and the calculations were conducted on a computer. The Cranston method of calculating pore size distribution assumes that the surface area in pores larger than 300 Å in diameter is insignificant compared to the surface area of pores less than 300 Å. Although the calculations with these samples cannot be made for pores less than 12 Å in diameter, the difference between nitrogen adsorption isotherms surface area calculations and surface area calculated by the Cranston method is due to the contributions of pores less than 12 Å in diameter.

Figure 3 is a graph of cumulative surface area versus pore size for pores 70 Å in diameter and less as computed by the Cranston method for plain carbon and three impregnated carbons. Above 60 Å pore size, neither vapor nor solution impregnated methods had any significant effect on surface area, indicating that very little material was deposited in these larger pores.

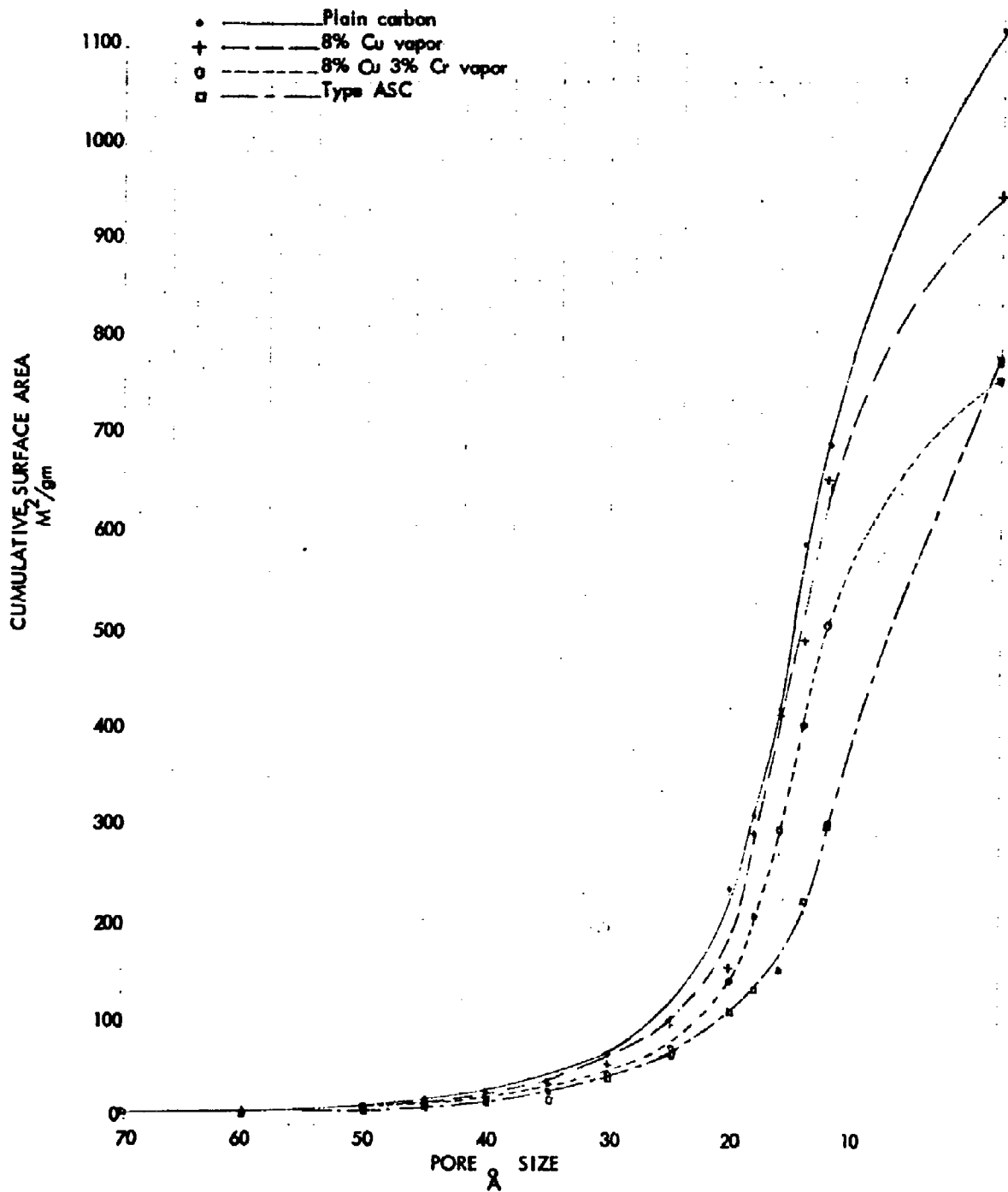
The graph for the 8% copper vapor impregnated sample shows a close approximation to the graph for a plain carbon sample down to pores 12 Å in diameter. This indicates that the small amount of material that was deposited in these pores formed an even coating. Below 12 Å in pore size, the graphs show different slopes. This is consistent with calculations of surface area which indicates that 95% of the vapor deposited copper is deposited in pores less than 12 Å in diameter. The subsequent deposition of chromium trioxide showed a shift in the curve indicating that a larger percentage of material was being deposited in pores 12 Å and above. Deposition is still quite uniform, since the copper-chromium vapor impregnated curve has a similar slope to that of the untreated carbon.

The curve for the solution impregnated type ASC carbon shows a distinctly different slope from graphs of the other samples, particularly in the pore size of 12 to 20 Å. Calculations of the surface area for this sample show that pores 12 Å in diameter and larger have a total surface area of 312.8 M<sup>2</sup>/gm compared to 697.1 M<sup>2</sup>/gm for the plain carbon, or a decrease of 55.1%. Pores less than 12 Å have a surface area of 475 M<sup>2</sup>/gm compared to 427.9 M<sup>2</sup>/gm for plain carbon, or a rise in surface area of 11%. This indicates that none of the material from solution impregnation is being deposited in pores less than 12 Å in diameter, and the graph further shows that the majority of material is deposited in pores between 12 and 20 Å.

#### 4.2.3 Electron Microscopic Examination

Scanning electron photomicrographs were taken of samples of 8% copper vapor impregnated carbon, 8% copper -3% chromium trioxide vapor impregnated carbon, type ASC solution impregnated carbon and untreated

Figure 3

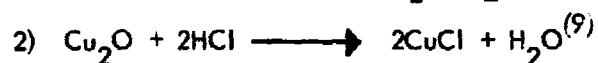
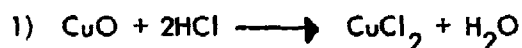


carbon. Samples of these photomicrographs can be seen in Fig. IV. The small white dots which appear on the surface in the various photographs are dust particles and not the coatings. The photomicrograph of untreated carbon shows cracks in the surface leading to interior pores, and sharply defined carbon crystallites. These same structures can be seen in the photomicrographs of the vapor impregnated samples, indicating that the impregnant deposited by this method forms such a thin even coating, that the carbon surface topography is altered to a very small extent. Surface cracks and carbon crystallites seem to be covered over in the photomicrograph of the ASC solution impregnated carbon, since this process tends to deposit more impregnant on the surface of the carbon particle.

#### 4.3 Detoxification Tests

##### 4.3.1 HCl Tests

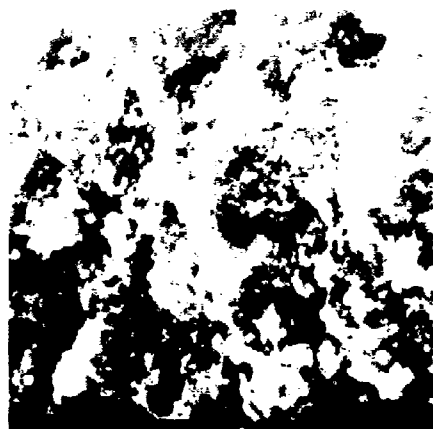
Previous tests had shown that the vapor deposition process deposits copper as the metal on the carbon surface and thus the copper must be oxidized to be effective against CK. A test based on the reaction of copper with HCl gas, was devised which would determine the degree of oxidation achieved by each treatment. At room temperature, copper +1 and +2 oxide reacts with HCl gas according to the following equations:



Thus one mole of copper as the +2 oxide would react with 2 moles of HCl while 1 mole of copper as the +1 oxide would only react with 1 mole of HCl. At room temperature, copper metal reacts very slowly with HCl. Therefore, the amount of HCl removed from a gas stream by an impregnated carbon is a measure of the oxidation state of the copper.

The apparatus used for the test can be seen in Fig. V. Reagent grade HCl gas is brought in through flowmeter 1, while breathing quality com-

FIGURE 4  
SCANNING ELECTRON PHOTOMICROGRAPHS OF VARIOUS CARBON SAMPLES



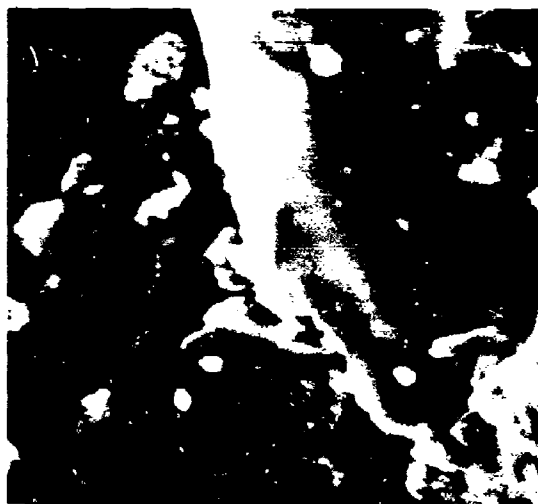
ASC WHETLERITE  
1000 X



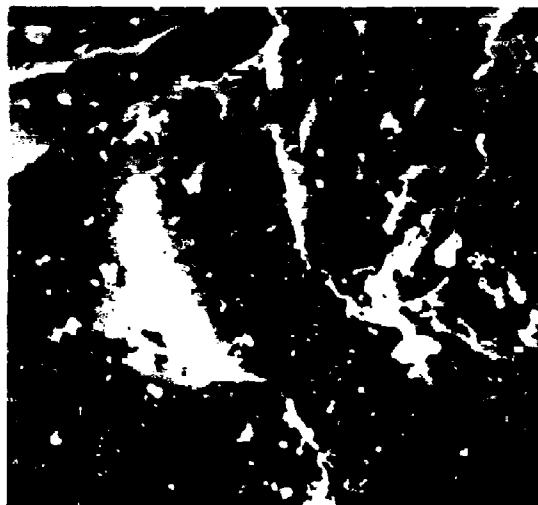
PLAIN CARBON  
1000 X



8% Cu VAPOR IMPREGNATED  
1000 X

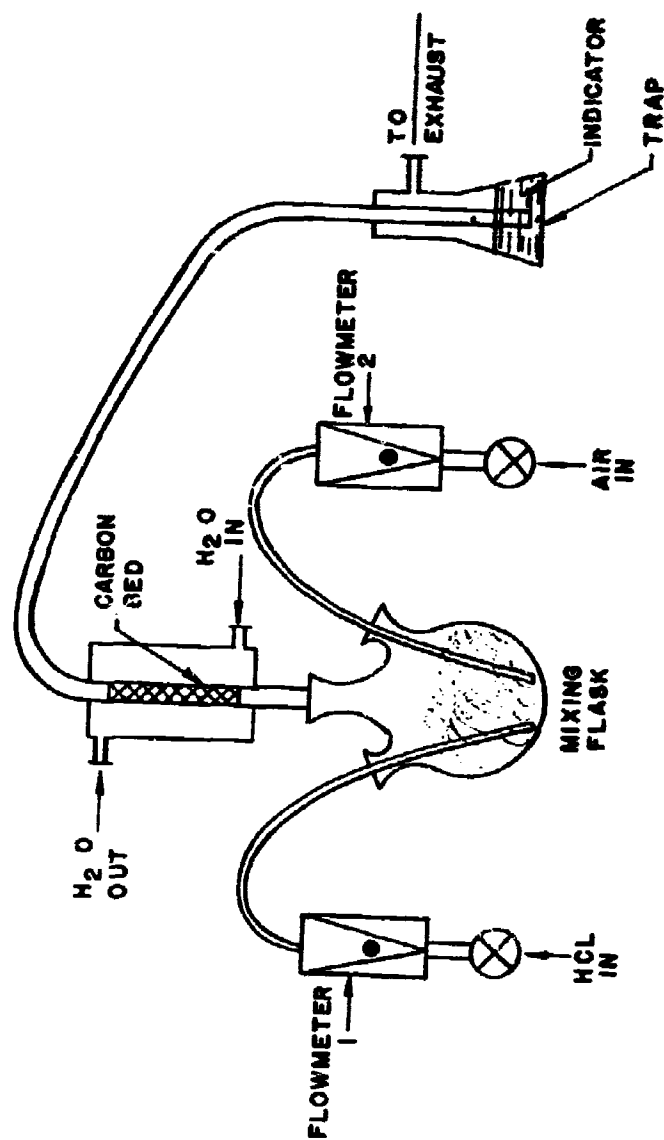


8% Cu VAPOR IMPREGNATED  
10,000 X



8% Cu VAPOR IMPREGNATED  
3,000 X

FIGURE V



HCL TEST APPARATUS



pressed air is bled in through flowmeter 2. Both gases enter the mixing flask containing glass wool to aid uniformity. From the mixing flask, the gases pass into the carbon bed which is maintained at a constant temperature by the circulation of water around the outside of the tube. When the carbon becomes saturated with HCl, excess gas passes into the trap containing a 0.04% solution of methyl orange indicator in 500 ml. of water. The break point is indicated by a change in color from orange to red. Operating conditions were:

Sample Tube area -  $1.04 \text{ cm}^2$   
Inlet concentration -  $0.50 \text{ g/l}$   
Volume flow -  $0.10 \text{ l/min.}$   
Linear velocity -  $96.2 \text{ cm/min.}$

Runs were made using untreated PCC grade CWS carbon, lot #8425C, as a means of comparing the effects of impregnated samples as well as a check on the performance of the system. All samples were heated in an oven at  $150^\circ\text{C}$  for 3 hours before testing in order to minimize the effects of adsorbed water on HCl pick up. Figure VI shows the results of the tests on blank carbon. The graph is linear and shows a minimum scattering of points, indicating that the system is sufficiently sensitive to yield meaningful data.

Table III is a summary of results of tests performed on samples of treated carbons. Each sample was heated to  $150^\circ\text{C}$  for 3 hr before testing and a minimum of 3 runs were performed on each sample. These samples represent each of the treatments given vapor impregnated samples as well as comparative tests on liquid impregnated types A and ASC carbons. The type A whetlerite is a laboratory prepared impregnation, while the type ASC is a sample of production run whetlerite supplied by Edgewood Arsenal.

Results were compared by two methods. First, the weight percent HCl adsorbed is calculated according to the formula:  $(\text{grams HCl per minute} \times \text{life}) \div \text{weight carbon} = \text{weight \% HCl adsorbed}$ . This allows for a direct comparison of samples by eliminating the effects of varying bed depth. Second, the % theoretical HCl pick up is calculated assuming the reaction #1 above. From this reaction, the theoretical HCl

FIG. VI HCL TEST

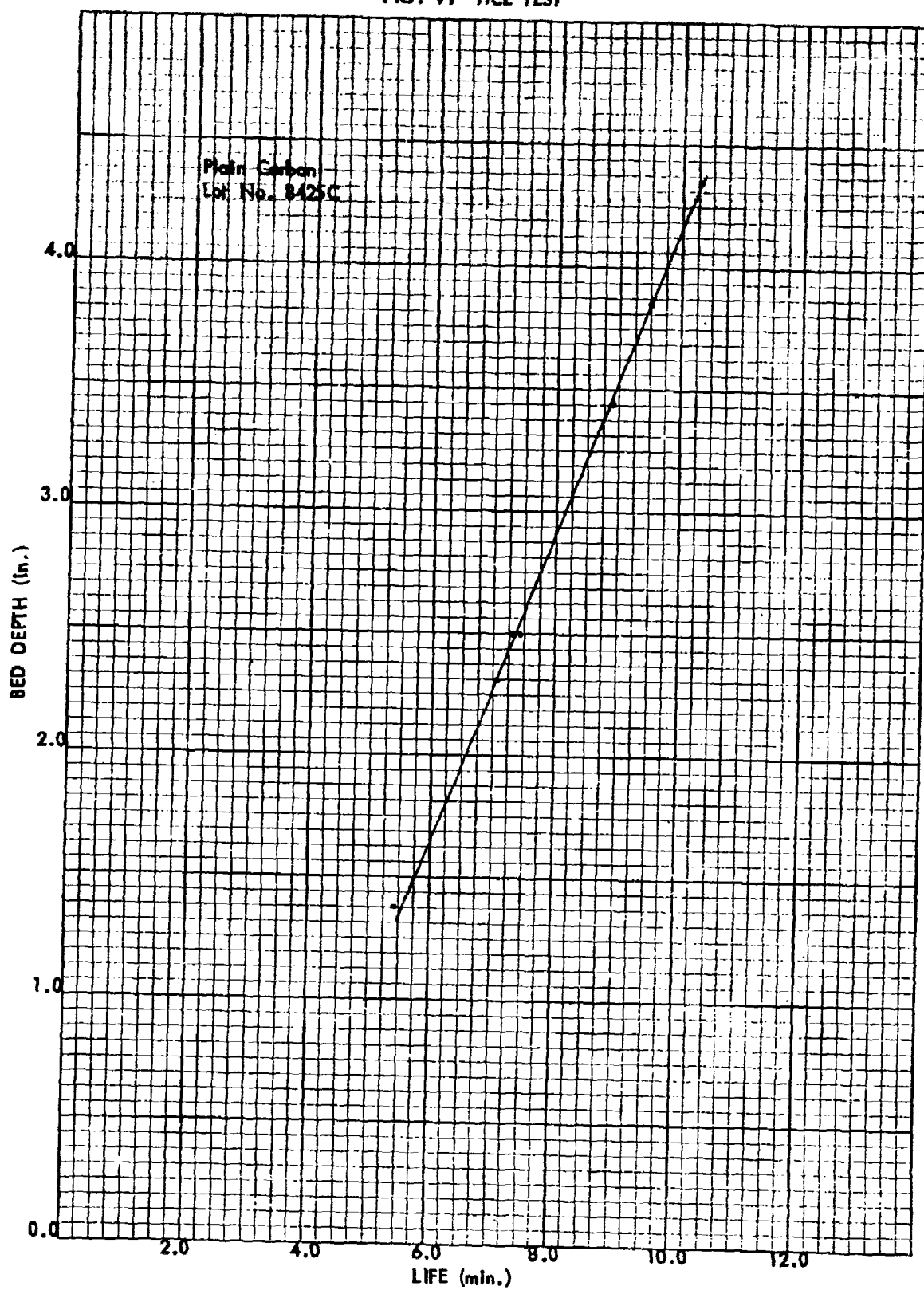


TABLE III

## HCl BREAKTHROUGH TEST

Run Number	Date	Carbon Weight gm	Life min	Bed Depth	Wt. % Adsorbed	% Theoretical HCl pick-up	Treatment
Control 8425C	4/24/69	3.24	8.87	3.46	13.7	--	150°C in Air
15-1/2% Cu	5/5/69	3.38	9.37	3.61	13.9	--	150°C in Air
14-2% Cu	5/5/69	3.40	9.92	3.51	14.6	61.5	150°C in Air
18-4% Cu	5/16/69	3.60	10.98	3.61	15.3	63.2	150°C in Air
19-4% Cu	5/27/69	3.50	10.42	3.53	14.9	55.5	150°C in Air
ASC Whetlerite	5/20/69	4.30	15.17	3.40	17.6	158.0	150°C in Air
Type A Whetlerite	5/1/69	4.17	14.87	3.48	17.8	155.0	150°C in
18(a) 4% Cu	5/21/69	3.70	11.02	3.52	14.9	69.5	O <sub>2</sub> at 30°C + NH <sub>3</sub> at room temp + 150°C in Air
20-4% Cu	5/29/69	3.74	11.04	3.53	14.8	64.0	O <sub>2</sub> at 80°C and 80 psi for 24 hr 150°C in Air
23-4% Cu	6/4/69	3.80	13.88	3.53	18.3	143.0	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> + 80°C + 100 psi for 24 hr 150°C in Air
26-4% Cu 1.5% CrO <sub>3</sub>	6/6/69	3.82	13.92	3.63	18.1	144.0	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> + 80°C + 100 psi for 24 hr 150°C in Air

pick up is equal to: (wt copper on carbon ÷ molecular weight copper) x molecular weight HCl. The theoretical HCl pick up is then divided into the amount of HCl adsorbed by the impregnated sample minus the amount adsorbed by the blank carbon, yielding the percent of theoretical pick up.

Tests on vapor impregnated carbons of 1/2, 2 and 4% by weight copper show an increase in weight % adsorbed with increasing copper concentration, as would be expected. Only a little over half of the theoretical amount of HCl, however, is adsorbed. This would indicate that complete oxidation of the copper to the +2 state is not achieved by heating the carbon to 150°C in air, and a more vigorous oxidation process is necessary.

Experiments made on type A and ASC whetlerite, showed a marked increase in weight percent adsorbed. In addition, these carbons picked up about 1-1/2 times the theoretical amount of HCl. The additional HCl is believed to have been picked up by ammonia which is either adsorbed on the carbon and not driven off by heating at 150°C, or is chemically combined in some form with the copper. These samples gave off a white cloud, believed to be  $\text{NH}_4\text{Cl}$ , just before break through. The results also show that the presence of chromium on the ASC does not significantly increase the HCl pick up when compared to the type A containing no chromium.

Based on these results, samples of 4% copper vapor impregnated carbons were treated in such a way as to promote complete oxidation of the copper and adsorption of ammonia. Samples 18(a) and 20 were subjected to oxidizing conditions and in addition the former was saturated with ammonia vapor. HCl tests of these samples however, failed to show any significant improvement over untreated impregnants, further indicating that ammonia must be chemically combined with copper on the whetlerite.

A high pressure treatment was chosen to produce the required copper-ammonia reaction. The copper impregnated carbon is placed in a steel tube lined with teflon and capped at one end. Powdered

ammonium carbonate is added to the tube and a cap, fitted with a 0 to 100 psi pressure gauge and a valve is threaded on the other end. The tube is then placed in an oven at  $80^{\circ}\text{C}$  for 24 hr. Ammonium carbonate decomposes above  $58^{\circ}\text{C}$  to produce  $\text{NH}_3$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  which are then free to react with the copper. Samples treated in this way (#23 and #26) resulted in an HCl pick up equal to that of a whetlerite, approximately 1-1/2 times that due to  $\text{Cu}^{+2}$  alone. Furthermore, vapor impregnation with chromium trioxide had no effect on the HCl activity as seen from sample 26.

#### 4.3.2 CK Tests

Tests for activity against toxic agents were conducted at Edgewood Arsenal using CK. Copper-chromium vapor impregnated carbons were compared with untreated carbons and with solution impregnated type ASC carbons. The solution impregnated carbons can remove three to four times the amount of CK that is removed by plain carbons. A complete list of the samples prepared including the various treatments given each sample, and a list of the toxic agent breakthrough tests parameters for the various samples, can be seen in Appendix II.

Initial samples of vapor impregnated Cu-Cr carbons failed to show any CK activity, although both metals were in the proper oxidation states. The vapor impregnation of Cu-Cr carbons with  $\text{NH}_3$  gas also failed to elicit any activity. In an attempt to pin point which compound was being deposited improperly, a sample of carbon, which has been impregnated with vapor copper, was solution impregnated with chromium trioxide and a carbon which had been solution impregnated with copper, was vapor impregnated with chromium. Neither sample produced significant CK activity.

Pore size distribution calculations concluded that vapor impregnated material was deposited, to a large extent in the small carbon pores, while solution impregnated material was unable to reach pores smaller than  $12 \text{ \AA}$ . A sample of vapor deposited copper was allowed to soak in a chromium trioxide whetlerite solution for 24 hr, in the belief

that some penetration of solution into pores less than  $12 \text{ \AA}$  will occur during this period of time. This sample showed significant CK activity.

HCl tests indicated the importance of  $\text{NH}_3$  to the activity of a whetlerite, but vapor impregnated carbon treated with  $\text{NH}_3$  failed to show activity due to reduction of the chrome from Cr +6 to Cr +3. Further tests revealed that this reduction was caused by the presence of a large excess of  $\text{NH}_3$  gas on the carbon during drying at  $150^\circ\text{C}$ , and could be controlled by maintaining a high ration of water to  $\text{NH}_3$  on the carbon.

The forementioned results led to the establishment of the following treatments necessary for the production of a vapor impregnated carbon with CK activity:

- 1) Vapor impregnate with copper from CuAA.
- 2) Oxidation of copper and combination with  $\text{NH}_3$  by exposure to  $\text{NH}_3$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at  $80^\circ\text{C}$  and 100 psi for 24 hr.
- 3) Removal of excess adsorbed gases by heating carbon to  $150^\circ\text{C}$  for 3 hr.
- 4) Vapor impregnation with chromium trioxide from chromyl chloride.
- 5) Vapor impregnation of carbon with small amount of  $\text{NH}_3$  followed by large amounts of  $\text{H}_2\text{O}$ .
- 6) Allow carbon to stand for 24 hr.
- 7) Dry carbon by heating to  $150^\circ\text{C}$  for 3 hr.

A sample of carbon treated in this manner produced activity against CK by removing more than twice as much agent as is removed by an untreated carbon.

## 5.0 CONCLUSIONS AND RECOMMENDATIONS

This program has demonstrated the feasibility of impregnating carbons with catalysts by vapor deposition techniques. Processes were developed for vapor impregnating carbons with four materials: copper, chromium tri-oxide, aluminum chloride and platinum. Tests performed on carbons, vapor impregnated with these materials, indicated that the coatings were uniform and in the proper oxidation state. Surface area measurements and pore size distribution calculations showed that vapor deposition processes deposit material in all carbon pores while solution processes do not penetrate pores less than 12 Å in diameter. As a result of this greater penetration, vapor processes cause a loss of surface area only half as great as that caused by solution processes.

Samples of copper-chromium vapor impregnated carbon which yielded activity against CK did not have the capacity of a type ASC whet-lerite; but they proved that the production of this type of carbon by vapor impregnation processes is very attractive. Due to the complexity of the copper-chromium, CK reaction and the large variation in impregnation parameters available through vapor deposition processes, additional efforts are necessary to achieve the optimum activity possible. These efforts should be directed along the following lines:

### 1) Chemical Activation Treatments

Results of HCl breakthrough tests revealed that ammonia was necessary for maximum activity. Additional agents such as  $O_2$  and  $CO_2$  may be beneficial, and the effect of treating copper-chromium vapor impregnated carbons with these agents should be investigated.

### 2) Copper-Chromium Concentration Variation

Past work with vapor impregnated copper-chromium carbons attempted to maintain the same concentration ratios of impregnants as was found on an ASC carbon. Surface area tests proved that twice as much impregnant could be deposited by the vapor process with no greater

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loss in surface area. Therefore, the optimum ratio of impregnants and total concentration possible for vapor impregnated carbons should be determined. This optimization alone should produce several orders of magnitude increase in protection over solution impregnated carbons.

### 3) Control of Impregnant Distribution

The deeper penetration and uniformity of coating distribution possible through vapor impregnation methods offers the potential of depositing material only in the pore sizes most effective for a particular agent. Studies of the effects of deposition parameters, such as pressure, temperature, etc., on coating distribution are necessary to develop this potential.

### 4) Survey of Various Types of Carbons

Vapor impregnation processes have demonstrated, by virtue of their ability to deposit material in small carbon pores, that carbons with large macropore area are not necessary for the production of successful impregnated carbons. Therefore, samples of different types of carbons should be impregnated and tested to determine the carbon most effectively vapor impregnated.

### 5) Aging Characteristics

Vapor impregnation techniques are sufficiently different from solution processes that different aging characteristics would be expected for the two processes. A survey of the aging characteristics of copper-chromium vapor impregnated carbons should be conducted to determine the process parameters which promote maximum storage life.

Investigation of these topics should allow vapor impregnation processes to reach their full potential and result in the production of an excellent carbon for toxic gas removal.



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# APPENDIX I

Sample Number	Treatment Conditions in Time Sequence	% Gas Adsorbed by Carbon	
		CK	PS
Control	None	0.77	47.2
PAC Lot 8425-C			
5	8% Cu *Vapor; 275°C, NH <sub>3</sub> , CO <sub>2</sub> , H <sub>2</sub> O	--	0.33
10	4% Cu Vapor; 275°C	--	44.7
14	2% Cu Vapor; 275°C	--	45.4
15	0.5% Cu Vapor; 275°C	--	45.4
188	4% Cu Vapor, 275°C, NH <sub>3</sub> , CO <sub>2</sub> , O <sub>2</sub> Sealed tube at 80°C for 24 hrs, 30 psi	--	44.3
12	8% Cu Vapor, 275°C, NH <sub>3</sub> , H <sub>2</sub> O; 3% Cr Vapor (CrO <sub>3</sub> ) 200 u, 155°C	0.28	41.0
13	8% Cu Vapor, 275°C NH <sub>3</sub> , H <sub>2</sub> O 2% Cr Vapor (CrO <sub>2</sub> Cl <sub>2</sub> ) Vac. 0°C NH <sub>3</sub> , H <sub>2</sub> O	0.16	41.6
10A	4% Cu Vapor, 275°C, 1.5% Cr, Soln Imp; Same NH <sub>4</sub> OH 1/2 Whetlerite	0.45	38.5
17	4% Cu Vapor, 275°C, 1.5% Cr Vapor (CrO <sub>2</sub> Cl <sub>2</sub> ) Vac 0°C NH <sub>3</sub> , H <sub>2</sub> O	0.31	32.9
16A	8% Cu, Soln Type A, Whetlerite, 2% Cr Vapor (CrO <sub>2</sub> Cl <sub>2</sub> ) Vac 0°C, NH <sub>3</sub> , H <sub>2</sub> O	0.41	18.9
24	4% Cu Vapor, 275°C, NH <sub>3</sub> , H <sub>2</sub> O, 3% H <sub>2</sub> O <sub>2</sub> , CO <sub>2</sub> , Heated 150°C for 3 hrs, 1% Cr Vapor, CrO <sub>2</sub> Cl <sub>2</sub> , Vac 0°C	0.24	--
28	1.5% Cr Vapor (CrO <sub>2</sub> Cl <sub>2</sub> ) Vac 0°C, NH <sub>3</sub> , H <sub>2</sub> O, 4% Cu Vapor, 275°C, NH <sub>3</sub> , H <sub>2</sub> O, 150°C 3 hrs	0.25	--
29	4% Cu Vapor, 275°C, CO <sub>2</sub> , H <sub>2</sub> O, NH <sub>3</sub> , 150°C 3 hrs 1% Cr Vapor dicumene chromium, 350°C	0.46	--
38	4% Cu Vapor, 275°C, (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> , 80°C 24 hrs O <sub>2</sub> R.T., 1% Cr Soln Soaked in Whetlerite 24 hrs	2.30	--
40	4% Cu Vapor, 275°C, NH <sub>4</sub> OH, H <sub>2</sub> O, 275°C, 2% Cr Vapor Dicumene Chromium, (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> , solid, 100°C, 100 psi 40 psi, O <sub>2</sub> , 24 hrs	0.96	--
39	4% Cu Vapor, NH <sub>4</sub> OH, CO <sub>2</sub> , H <sub>2</sub> O, 275°C, 2% Cr Vapor Dicumene Chromium, 350°C, boiled in 30% H <sub>2</sub> O <sub>2</sub>	1.11	--

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# APPENDIX I

Sample Number	Treatment Conditions in Time Sequence	% Gas Adsorbed by Carbon	
		CR	PS
19A	4% Cu Vapor, 275°C, 1.5% Cr Soln (Whetlerite)	0.37	--
25	Soln, Type AC Whetlerite	3.16	--
26	4% Cu Vapor, 275°C, $(\text{NH}_4)_2\text{CO}_3$ , Saturated 100 psi vacuum dried at R.T., 1% Cr Vapor ( $\text{CrO}_2\text{Cl}_2$ ) 0°C, $\text{NH}_3$ , $\text{H}_2\text{O}$ , Saturated Vapor Phase	0.33	--
42	4% Cu Vapor, 275°C, 3% Cr Soln, Soaked 24 hrs, Whetlerite	1.65	--
45	4% Cu Vapor, 275°C, 2% Cr Vapor ( $\text{CrO}_2\text{Cl}_2$ ) - 70°C ( $\text{NH}_4$ ) $_2\text{CO}_3$ , sealed tube, 80°C, 100 psi 24 hrs	0.48	--
46	4% Cu Vapor, 275°C, $(\text{NH}_4)_2\text{CO}_3$ , sealed tube, 80°C, 100 psi 24 hrs, 150°C 3 hrs, 2% Cr Vapor ( $\text{CrO}_2\text{Cl}_2$ ), 70°C ( $\text{NH}_4$ ) $_2\text{CO}_3$ , sealed tube, 30°C, 100 psi, 24 hrs	0.25	--
48	4% Cu Vapor, 275°C, $(\text{NH}_4)_2\text{CO}_3$ , sealed tube, 80°C, 100 psi Vacuum dried R.T., 3% Cr Vapor ( $\text{CrO}_2\text{Cl}_2$ ) ( $\text{NH}_4$ ) $_2\text{CO}_3$ sealed tube 80°C, 100 psi, 24 hrs	0.48	28.9
52	4% Cu Vapor, 275°C, $(\text{NH}_4)_2\text{CO}_3$ , sealed tube, 80°C, 100 psi 24 hrs, 3% Cr Soln Whetlerite, 24 hrs	2.55	31.6
53	3% Cr Vapor, ( $\text{CrO}_2\text{Cl}_2$ ), $\text{NH}_4\text{OH}$ , $\text{H}_2\text{O}$ , 150°C, 3 hrs	0.60	44.7
54	3% Cr Soln, Whetlerite	0.52	--
59	4% Cu, 1% Cr, Solution Impregnation, $\text{Cu}(\text{NO}_3)_2 + \text{CrO}_3 + \text{H}_2\text{O}$	0.05	--
61	4% Cu Vapor, 275°C, 2% Cr Whetlerite, 24 hr soak	1.60	--
62	4% Cu Vapor, 275°C ( $\text{NH}_4$ ) $_2\text{CO}_3$ , 80°C at 100 psi, dried 150°C 3 hrs 1.5% Cr Vapor, $\text{CrO}_2\text{Cl}_2 + \text{H}_2\text{O}$ , 16 hrs	0.03	--
63	4% Cu Vapor, 275°C ( $\text{NH}_4$ ) $_2\text{CO}_3$ , 80°C, at 100 psi, + 150°C, 3 hrs, 1.5% Cr Vapor, $\text{CrO}_2\text{Cl}_2 + \text{large excess } \text{H}_2\text{O} + \text{NH}_3 + 16 \text{ hrs soak}$	1.58	--
64	4% Cu Vapor, 275°C + ( $\text{NH}_4$ ) $_2\text{CO}_3$ , 80°C, 100 psi, Vacuum dried 60°C, 1.5% Cr Vapor, $\text{CrO}_2\text{Cl}_2 + \text{H}_2\text{O}$	0.63	--
66	4% Cu Vapor, 275°C (Steamed) $\text{CO}_2$ 60 psi, 24 hrs, heated 150°C for 3 hrs, 1.5% Cr Vapor, $\text{CrO}_2\text{Cl}_2 + \text{H}_2\text{O}$	0.20	--

# APPENDIX I

Sample Number	Treatment Conditions In Time Sequence	% Gas Adsorbed by Carbon	
		CK	PS
67	4% Cu Vapor, 275°C (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> , 80°C, 100 psi Dried 150°C 3 hrs 1.5% Cr Vapor, CrO <sub>2</sub> Cl <sub>2</sub> + H <sub>2</sub> O + NH <sub>3</sub> 24 hr soak	.58 .58	-- --
68	4% Cu Vapor, 275°C (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> , 80°C at 100 psi Dried, 150°C for 3 hrs, 1.5% Cr Vapor CrO <sub>2</sub> Cl <sub>2</sub> + H <sub>2</sub> O, 24 hr soak	.13	--
69A	4% Cu Vapor, 275°C (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> , 80°C, 100 psi, Dried at room temperature in vacuum, 1.5% Cr Vapor CrO <sub>2</sub> Cl <sub>2</sub> + H <sub>2</sub> O + NH <sub>3</sub> , 24 hr soak	.25	--
70	4% Cu Vapor, 275°C, (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> , 80°C, 100 psi, Dried at room temperature in vacuum, 1.5% Cr Vapor CrO <sub>2</sub> Cl <sub>2</sub>	.20	--
71	4% Cu Vapor, 275°C, CO <sub>2</sub> , 80°C, 100 psi, Dried at 150°C, 3 hrs, 1.5% Cr Vapor, Cr Vapor, CrO <sub>2</sub> Cl <sub>2</sub> + H <sub>2</sub> O + NH <sub>3</sub> 24 hr soak	.99	--
72	4% Cu Vapor, 275°C, O <sub>2</sub> , 80°C at 100 psi, Dried at 150°C, 3 hrs, 1.5% Cr Vapor, CrO <sub>2</sub> Cl <sub>2</sub> + H <sub>2</sub> O NH <sub>3</sub> , 24 hr soak	.78	--
75A	8% Cu Vapor, 275°C, (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> , 80°C, 100 psi, dried 150°C 3 hrs, 1.5% Cr Vapor, CrO <sub>2</sub> Cl <sub>2</sub> + H <sub>2</sub> O + NH <sub>3</sub> 24 hr soak	.75	--
76	8% Cu Vapor, 275°C, (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> , 80°C, 100 psi, Dried 150°C 3 hrs, 3% Cr Vapor, CrO <sub>2</sub> Cl <sub>2</sub> + H <sub>2</sub> O + NH <sub>3</sub> 24 hrs soak	1.76	--
77	4% Cu Vapor, 275°C (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> , 80°C, 100 psi Dried 150°C, 3 hrs, 1.5% Cr Vapor, CrO <sub>2</sub> Cl <sub>2</sub> + H <sub>2</sub> O + NH <sub>3</sub> , 24 hr soak	2.42	--
78	4% Cu Vapor, 275°C (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> , 80°C, 100 psi, Dried 150°C, 3 hrs, 3% Cr Vapor, CrO <sub>2</sub> Cl <sub>2</sub> + H <sub>2</sub> O + NH <sub>3</sub> , 24 hr soak	1.00	--

\* Cu vapor deposited on carbon from copper acetylacetonate.

NOTE: All treated samples received a final cure of heating in air at 150°C for 3 hours.

# APPENDIX

## EDGEWOOD ARSENAL BREAKTHROUGH TIME TESTS FOR VARIOUS IMPREGNATED CARBONS USING CK

Sample No.	Date	Inlet Conc. mg/L	Relative Humidity	Dry Bulb Temp.	Velocity cm/min	Volume Flow L/min	Carbon Volume cm	Carbon Weight g	Protective Life Min. As is corrected	Bed Depth cm	Gas
Control											
8425C PCC	3/12/69	4.12	80	80	575	1.675	15.0	6.10	5.6	5.77	CK
8425C PCC	3/12/69	4.12	80	80	575	1.675	15.0	5.91	5.5	5.66	CK
8425C PCC	3/12/69	4.08	80	80	575	1.675	30.0	11.40	23.2	24.6	CK
8425C PCC	3/12/69	4.27	80	80	575	1.675	30.0	12.3	24.7	25.2	CK
8425C PCC	3/12/69	4.08	80	80	575	1.675	7.5	2.79	1.5	1.5	CK
8425C PCC	3/12/69	4.08	80	80	575	1.675	7.5	2.72	1.5	1.5	CK
8425C PCC	3/12/69	4.08	80	80	575	1.675	22.5	9.56	14.4	14.63	CK
8425C PCC	3/12/69	4.08	80	80	575	1.675	22.5	8.87	12.2	12.67	CK
II-12 - 3/5											
P-I(8)Cu(3)Cr	3/18/69	4.28	80	84	575	1.68	10.0	5.22	1.7	1.8	CK
II-12 - 3/5											
P-I(8)Cu(3)Cr	3/18/69	4.28	80	84	575	1.68	10.0	4.65	1.9	2.0	CK
II-12 - 3/5											
P-I(8)Cu(3)Cr	3/18/69	49.88	0	--	365	1.07	10.0	5.37	32.0	32.1	PS
II-13 - 3/6											
P-I(8)Cu(2)Cr	3/18/69	4.28	80	84	575	1.68	10.0	5.24	1.1	1.18	CK
II-13 - 3/6											
P-I(8)Cu(2)Cr	3/20/69	4.28	80	84	575	1.68	10.0	4.85	1.0	1.07	CK
Control											
8425C PCC	3/20/69	49.88	0	--	365	1.07	10.0	3.76	36.4	39.2	PS
Control											
8425C PCC	3/20/69	49.88	0	--	365	1.07	10.0	2.51	17.2	19.5	PS

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# APPENDIX

## EDGEWOOD ARSENAL BREAKTHROUGH TIME TESTS FOR VARIOUS IMPREGNATED CARBONS USING CK

Sample No.	Date	Inlet Conc. mg/L	Relative Humidity	Dry Bulb Temp.	Velocity cm/min	Volume Flow L/min	Carbon Volume cm	Carbon Weight g	Protective Life Min. As is corrected	Bed Depth cm	Gas
Control											
8425C PCC	4/1/69	50.01	50	75	365	1.07	7.5	2.91	26.6	26.6	PS
8425C PCC	4/1/69	50.01	50	75	365	1.07	7.5	3.05	28.6	28.6	PS
CS-I-II 5-2/17 P-I (8) Cu	4/1/69	50.01	50	75	365	1.07	10.0	4.69	0.3	0.3	PS
CS-I-II 5-2/17 P-I (8) Cu	4/1/69	50.01	50	75	365	1.07	10.0	5.05	0.3	0.3	PS
CS-I-II 10-3/4 P-I (4) Cu	4/1/69	50.01	50	75	365	1.07	10.0	4.29	36.6	36.6	PS
CS-I-II 10-3/4 P-I (4) Cu	4/1/69	50.01	50	75	365	1.07	10.0	4.61	37.8	37.8	PS
CS-I-II 10-3/4 P-I (4) Cu (1.5) Gr NH <sub>4</sub> OH	4/1/69	50.01	50	75	365	1.07	7.5	3.50	25.3	25.3	PS
CS-I-II 10-3/4 P-I (4) Cu (1.5) Gr NH <sub>4</sub> OH	4/1/69	50.01	50	75	365	1.07	7.5	3.50	25.2	25.2	PS
CS-I-II 10-3/4 P-I (4) Cu (1.5) Gr NH <sub>4</sub> OH	4/2/69	4.22	80	80	575	1.68	10.0	4.52	2.8	2.9	CK
CS-I-II 10-3/4 P-I (4) Cu (1.5) Gr NH <sub>4</sub> OH	4/2/69	4.22	80	80	575	1.68	10.0	4.65	2.7	2.8	CK
8425C PCC	4/2/69	4.22	80	80	575	1.68	10.0	4.05	2.3	2.4	CK
8425C PCC	4/2/69	4.22	80	80	575	1.68	10.0	3.90	2.1	2.1	CK

\*Bed Area is 2.92 cm<sup>2</sup>.

\*Bed Area is 2.93 cm<sup>2</sup>.

A. PENDIX  
EDGEWOOD ARSENAL BREAKTHROUGH TIME TESTS FOR VARIOUS IMPREGNATED CARBONS

Sample No.	Date	Inlet Conc. mg./l.	Relative Humidity	Dry Bulb Temp.	Velocity cm./min	Volume Flow L/min	Carbon Volume cm <sup>3</sup>	Carbon Weight g	Protective Life		Bed Depth cm	Gas
									As is	corrected		
CS1-II 14-3/24 P-I (2) Cu	4/16/69	50.48	48	78	365	1.07	10.0	4.27	35.5	35.15	3.4	PS
CS1-II 14-3/24 P-I (2) Cu	4/16/69	50.48	48	78	365	1.07	10.0	4.50	38.2	37.82	3.4	PS
CS1-II 15-3/31 P-I (1/2) Cu	4/16/69	50.48	48	78	365	1.07	10.0	3.86	33.2	32.87	3.4	PS
CS1-II 15-3/31 P-I (1/2) Cu	4/16/69	50.48	48	78	365	1.07	10.0	4.46	35.2	34.85	3.6	PS
Sol. Imp. Carbon 4/7/69	4/16/69	50.48	48	78	365	1.07	10.0	5.39	29.3	29.01	3.7	PS
Sol. Imp. Carbon 4/7/69	4/16/69	50.48	48	78	365	1.07	10.0	5.37	33.5	33.16	3.6	PS
8425C PCC	4/16/69	50.48	48	78	365	1.07	5.0	2.00	16.6	16.43	1.9	PS
8425C PCC	4/16/69	50.48	48	78	365	1.07	7.5	3.21	30.5	30.19	2.6	PS
8425C PCC	4/21/69	3.66	75	67	575	1.68	10.0	4.41	2.5	2.73	3.4	CK
8425C PCC	4/21/69	3.66	75	67	575	1.68	10.0	4.65	2.6	2.84	3.5	CK
Sol. Imp. Carbon 4/7/69	4/21/69	3.66	75	67	575	1.68	10.0	5.31	14.6	15.95	3.5	CK
Sol. Imp. Carbon 4/7/69	4/21/69	3.66	75	67	575	1.68	10.0	4.91	20.0	21.86	3.4	CK
8425C PCC	4/25/69	3.80	70	66	575	1.68	22.5	9.13	26.0	24.70	7.5	CK
8425C PCC 4/7/69	4/25/69	3.975	80	66	575	1.68	10.0	5.55	52.7	52.38	3.4	CK
Sol. Imp. AC Carbon 4/7/69	4/25/69	3.975	80	66	575	1.68	10.0	5.02	39.2	38.96	3.4	CK

\*Bed Area is 2.93 cm<sup>2</sup>.

APPENDIX  
EDGEWOOD ARSENAL BREAKTHROUGH TIME TESTS FOR VARIOUS IMPREGNATED CARBONS

Sample No.	Date	Inlet Conc. mg/L	Relative Humidity	Dry Bulb Temp.	Velocity cm/min	Volum. Flow L/min	Carbon Volume cm <sup>3</sup>	Carbon Weight g	Protective Life Min. As is corrected	Bed Depth cm	Gas
II-17-5/6 P-1 (4) 1.5 Cr Vapor Imp. 4%Cu 1.5% Cr	5/8/69	3.80	80	78	575	1.68	10.0	4.99	2.6	2.47	3.2 CK
II-17-5/6 P-1(4)Cu 1.5 Cr. Vapor Imp. 4%Cu 1.5% Cr	5/8/69	3.80	80	78	575	1.68	10.0	4.67	2.1	2.00	3.1 CK
II-16-5/5 P-1(8)Cu <sub>3</sub> Cr Sol. Imp. Cu Vapor Imp. Cr	5/8/69	3.80	80	78	575	1.68	10.0	5.11	3.6	3.42	3.2 CK
II-16-5/5 P-1(8)Cu <sub>3</sub> Cr Sol. Imp. Cu Vapor Imp. Cr	5/8/69	3.80	80	78	575	1.68	10.0	4.33	2.6	2.47	3.2 CK
8425C PCC	5/8/69	3.80	80	78	575	1.68	20.0	8.18	12.5	11.87	6.8 CK
8425C PCC	5/8/69	3.80	80	78	575	1.68	20.0	8.66	10.5	9.98	6.7 CK
8425C PCC	5/14/69	51.09	48	78	365	1.07	5.0	2.14	16.7	17.0	1.9 PS
II-16-5/5 P-A(8)Cu <sub>3</sub> Cr Sol. Imp. Cu Vapor Imp. Cr	5/14/69	51.09	48	78	365	1.07	5.0	2.81	9.4	9.5	1.8 PS
II-16-5/5 P-A(8)Cu <sub>3</sub> Cr Sol. Imp. Cu Vapor Imp. Cr	5/14/69	51.09	48	78	365	1.07	5.0	2.50	8.9	9.0	1.9 PS
II-17 5/6 P-1(4)Cr 1.5Cr Vapor Imp. 4%Cu 1.5% Cr	5/14/69	51.09	48	78	365	1.07	5.0	2.45	14.1	14.3	1.8 PS
II-17 5/6 P-1(4)Cr 1.5Cr Vapor Imp. 4%Cu 1.5%Cr	5/14/69	51.09	48	78	365	1.07	5.0	2.38	15.5	15.8	1.9 PS
8425C PCC	5/20/69	4.07	80	73	575	1.68	20.0	8.51	12.0	12.2	7.1 CK
8425C PCC	5/20/69	4.07	80	73	575	1.68	20.0	8.27	11.8	12.0	7.2 CK
II-19 5/15 P-1 1/2Cu, 1/2Cr	5/20/69	4.07	80	73	575	1.68	10.0	4.40	4.4	4.5	3.5 CK
II-19 5/15 P-1 1/2Cu, 1/2Cr	5/20/69	4.07	80	73	575	1.68	10.0	4.21	3.2	3.3	3.5 CK



\*Bed Area is 2.93 cm<sup>2</sup>.

APPENDIX  
EDGEWOOD ARSENAL BREAKTHROUGH TIME TESTS FOR VARIOUS IMPREGNATED CARBONS

Sample No.	Date	Inlet Conc. mg/L	Relative Humidity	Dry Bulb Temp.	Velocity cm/min	Volume Flow L/min	Carbon Volume cm <sup>3</sup>	Carbon Weight g	Protective Life		Bed Depth cm	Gas
									Min	As is corrected		
Control												
8425C FCC	7/10/69	4.16	80	79	575	1.68	20.0	8.23	7.4	7.6	6.8	CK
8425C PCC	7/10/69	4.16	80	79	575	1.68	20.0	8.22	8.1	8.4	6.5	CK
II-29 6/17/69 (4) Cu (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> (1Gr)	7/10/69	4.16	80	79	575	1.68	10.0	4.93	1.2	1.2	3.7	CK
II-29 6/17/69 (4) Cu (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> (1Gr)	7/10/69	4.16	80	79	575	1.68	10.0	4.96	1.2	1.2	3.7	CK
II-38 6/26/69 (4) Cu (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> + liq. Gr	7/10/69	4.16	80	79	575	1.68	20.0	10.60	32.4	33.6	6.6	CK
II-38 6/26/69 (4) Cu (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> + liq. Gr	7/11/69	4.36	80	77	575	1.68	20.0	10.59	35.2	38.1	6.6	CK
II-39 6/24/69 (4) Cu (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> (2)Gr H <sub>2</sub> O <sub>2</sub>	7/14/69	4.16	80	79	575	1.68	20.0	9.66	15.5	16.1	6.9	CK
II-39 6/24/69 (4) Cu (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> (2)Gr H <sub>2</sub> O <sub>2</sub>	7/14/69	4.38	80	77	575	1.68	20.0	9.41	14.0	15.2	6.7	CK
II-40 6/27/69 (4) Cu (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> (2)Gr	7/16/69	4.16	80	79	575	1.68	20.0	10.67	14.4	14.9	7.0	CK
II-40 6/27/69 (4) Cu (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> (2)Gr	7/16/69	4.16	80	79	575	1.68	20.0	10.36	14.7	15.2	6.8	CK
8425C PCC	7/11/69	4.36	80	77	575	1.68	20.0	8.51	10.0	10.9	6.6	CK
8425C PCC	7/11/69	4.36	80	77	575	1.68	20.0	8.50	9.2	10.0	6.8	CK

# APPENDIX

## EDGEWOOD ARSENAL BREAKTHROUGH TIME TESTS FOR VARIOUS IMPREGNATED CARBONS USING CK

Sample No.	Date	Inlet Conc. mg/L	Relative Humidity	Dry Bulb Temp.	Velocity cm/min	Volume Flow L/min	Carbon Volume cm	Carbon Weight g	Protective Life Min. As is corrected	Bed Depth cm	Gas
Control											
8425C PCC	9/23/69	3.78	80	76	575	1.68	20.0	7.7	7.5	7.1	6.5 CK
II-42 9/8/69 (4)Cu (3)Gr Sol. Imp.	9/23/69	3.90	80	76	575	1.68	20.0	9.81	24.3	23.8	7.5 CK
II-42 9/8/69 (4)Cu (3)Gr Sol. Imp.	9/23/69	3.90	80	76	575	1.68	20.0	9.65	25.8	25.2	7.1 CK
II-45 9/9/69 (4)Cu (2)Gr (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	9/23/69	3.90	80	76	575	1.68	20.0	9.16	6.2	6.0	7.0 CK
II-45 9/9/69 (4)Cu (2)Gr (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	9/23/69	3.90	80	76	575	1.68	20.0	10.31	7.0	6.8	7.5 CK
II-46 9/10/69 (4)Cu 2Gr (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	9/23/69	3.90	80	76	575	1.68	20.0	9.21	4.0	3.9	6.5 CK
II-46 9/10/69 (4)Cu 2Gr (NH <sub>4</sub> ) <sub>2</sub> CO	9/23/69	3.90	80	76	575	1.68	20.0	9.67	3.4	3.3	6.5 CK
8425C PCC	9/23/69	3.90	80	76	575	1.68	20.0	8.20	7.4	7.3	6.5 CK

\*Bed Area is 2.93 cm<sup>2</sup>.

# APPENDIX

## EDGEWOOD ARSENAL BREAKTHROUGH TIME TESTS FOR VARIOUS IMPREGNATED CARBONS USING CK

Sample No.	Date	Inlet Conc. mg/L	Relative Humidity	Dry Bulb Temp.	Velocity cm/min	Volume Flow L/min	Carbon Volume cm	Carbon Weight g	Protective Life Min. $\bar{P}$ is corrected	Bed Depth cm	Gas
Control 8425C	9/30/69	4.08	80	80	575	1.68	20.0	7.36	5.6	5.7	6.1 CK
II-48 9/12/69 4%Cu(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> 3%Cr(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	9/30/69	4.08	80	80	575	1.68	20.0	10.21	7.2	7.3	7.3 CK
II-48 9/12/69 4%Cu(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> 3%Cr(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	9/30/69	4.08	80	80	575	1.68	20.0	10.53	7.8	7.9	7.3 CK
II-52 9/16/69 4%Cu(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> Cr Solution 24 hrs	9/30/69	4.08	80	80	575	1.68	20.0	10.09	37.9	38.7	7.4 CK
II-52 9/16/69 4%Cu(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> Cr Solution 24 hrs	9/30/69	4.08	80	80	575	1.68	20.0	10.23	38.0	38.7	7.4 CK
II-53 9/19/69 3%Cr vapor deposition NH <sub>4</sub> OH, H <sub>2</sub> O	9/30/69	4.08	80	80	575	1.68	20.0	8.97	9.1	9.2	7.0 CK
II-53 9/19/69 3%Cr vapor deposition NH <sub>4</sub> OH, H <sub>2</sub> O	9/30/69	4.08	80	80	575	1.68	20.0	9.02	7.3	7.4	7.5 CK
II-54 9/22/69 3%Cr Whetlerite sol.	9/30/69	4.08	80	80	575	1.68	20.0	9.40	8.5	8.6	7.0 CK
II-54 9/22/69 3%Cr Whetlerite sol.	9/30/69	4.08	80	80	575	1.68	20.0	9.75	6.0	6.1	6.5 CK
Control 8425C	9/30/69	4.08	80	80	575	1.68	20.0	8.20	7.3	7.4	6.4 CK

# APPENDIX

## EDGEWOOD ARSENAL BREAKTHROUGH TIME TESTS FOR VARIOUS IMPREGNATED CARBONS USING CK

Sample No.	Date	Inlet Conc. mg/L	Relative Humidity	Dry Bulb Temp.	Velocity cm/min	Volume Flow L/min	Carbon Vol% cm	Carbon Weight g	Protective Life Min. As is corrected	Bed Depth cm	Gas
Control											
8425C PCC	11/4/69	4.04	80	80	575	1.68	10.0	4.12	3.8	3.2	CK
8425C PCC	11/4/69	4.04	80	80	575	1.68	10.0	4.26	3.6	3.3	CK
11-58 10/13/69	11/4/69	4.04	80	80	575	1.68	10.0	4.33	4.5	3.3	CK
11-58 10/13/69	11/4/69	4.04	80	80	575	1.68	10.0	3.97	4.4	3.2	CK
11-59 10/15/69	11/4/69	4.04	80	80	575	1.68	10.0	5.73	0.3	3.4	CK
11-59 10/15/69	11/4/69	4.04	80	80	575	1.68	10.0	5.82	0.4	3.3	CK
8425C PCC	11/18/69	4.27	80	79	575	1.68	20.0	8.66	9.3	6.4	CK
8425C PCC	11/18/69	4.27	80	79	575	1.68	20.0	7.90	10.8	6.4	CK
11-61 11/6/69 (4)Cu (2)Cr	11/18/69	4.27	80	79	575	1.68	20.0	10.04	19.5	6.5	CK
11-61 11/6/69 (4)Cu (2)Cr	11/18/69	4.27	80	79	575	1.68	20.0	10.08	22.5	6.9	CK
11-62 11/10/69 (4)Cu (1.5)Cr	11/18/69	4.27	80	79	575	1.68	20.0	9.94	3.8	7.1	CK
11-62 11/10/69 (4)Cu (1.5)Cr	11/18/69	4.27	80	79	575	1.68	20.0	9.53	3.4	6.6	CK
11-63 11/11/69	11/18/69	4.27	80	79	575	1.68	20.0	9.90	20.1	7.0	CK

\*Bed Area is 2.93 cm<sup>2</sup>.

# APPENDIX

EDGEWOOD ARSENAL BREAKTHROUGH TIME TESTS FOR VARIOUS IMPREGNATED CARBONS USING CK

Sample No.	Date	Inlet Conc. mg/L	Relative Humidity	Dry Bulb Temp.	Velocity cm/min	Volume Flow L/min	Carbon Vol% cm	Carbon Weight g	Protective Life		Bed Depth cm	Gas
									Min.	As is corrected		
Control												
8425C	11/23/69	4.16	80	80	575	1.68	20.0	7.82	10.0	10.4	6.4	CK
8425C	11/23/69	4.16	80	80	575	1.68	20.0	7.99	9.9	10.3	6.5	CK
II-64 11/13/69 4%Cr 1.5%Cr	11/23/69	4.16	80	80	575	1.68	20.0	9.98	9.3	9.6	6.6	CK
II-64 11/13/69 4% Cr 1.5% Cr	11/23/69	4.16	80	80	575	1.68	20.0	9.31	8.0	8.3	6.4	CK
II-66 11/18/69 4%Cu 1.5%Cr CO <sub>2</sub>	11/23/69	4.16	80	80	575	1.68	20.0	11.41	3.0	3.1	7.1	CK
II-66 11/18/69 4%Cu 1.5%Cr CO <sub>2</sub>	11/23/69	3.66	80	80	575	1.68	20.0	9.88	3.0	3.1	6.6	CK
Control												
8425C	1/2/70	3.66	80	80	575	1.68	20.0	8.63	15.0	14.3	7.2	CK
8425C	1/2/70	3.66	80	80	575	1.68	20.0	7.93	11.8	10.7	6.5	CK
II-65 12/4/69 4%Cu 1.5% Cr	1/4/70	3.66	80	80	575	1.68	20.0	4.95	3.6	3.2	6.8	CK
II-65 12/4/69 4%Cu 1.5% Cr	1/12/70	3.66	80	80	575	1.68	20.0	10.55	3.8	3.4	6.9	CK
II-67 12/17/69 4%Cu 1.5%Cr	1/12/70	3.66	80	80	575	1.68	20.0	10.20	9.7	8.8	7.0	CK
II-67 12/17/69 4%Cu 1.5%Cr	1/12/70	3.66	80	80	575	1.68	20.0	9.88	10.0	9.1	7.2	CK
II-68 12/18/69 4%Cu 1.5%Cr	1/12/70	3.66	80	80	575	1.68	20.0	11.20	2.6	2.3	7.4	CK
II-68 12/18/69 4%Cu 1.5%Cr	1/12/70	3.66	80	80	575	1.68	20.0	11.45	2.6	2.3	7.3	CK
II-70 12/19/69 4%Cu 1.5%Cr	1/12/70	3.66	80	80	575	1.68	20.0	10.90	3.7	3.3	7.1	CK
II-70 12/19/69 4%Cu 1.5%Cr	1/12/70	3.66	80	80	575	1.68	20.0	10.66	3.8	3.4	6.9	CK

\*Bed Area is 2.93 cm<sup>2</sup>.

# APPENDIX EDGEWOOD ARSENAL BREAKTHROUGH TIME TESTS FOR VARIOUS IMPREGNATED CARBONS

Sample No.	Date	Inlet Conc. mg/L	Relative Humidity	Dry Bulb Temp. °C	Velocity cm/min	Volume Flow L/min	Carbon Volume cm	Carbon Weight g	Protective Life		Bed Depth cm	Gas
									Min	As is corrected		
Control 8425C	1/70	4.05	80	74	575	1.68	20.0	8.45	12.4	12.1	6.7	CK
8425C	1/70	3.90	80	74	575	1.68	20.0	8.53	11.4	11.5	6.6	CK
II-71 12/22/69 4%Cu(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> (3Cr)	1/70	3.90	80	74	575	1.68	20.0	9.98	13.6	13.3	7.0	CK
II-71 12/22/69 4%Cu(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> (3Cr)	1/70	4.05	80	74	575	1.68	20.0	9.69	15.6	15.7	6.7	CK
II-72 12/23/69 4%Cu(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> 1.5%Cr H <sub>2</sub> O <sub>2</sub>	1/70	3.90	80	74	575	1.68	20.0	9.65	10.4	10.2	6.7	CK
II-72 12/23/69 4%Cu(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> 1.5%Cr H <sub>2</sub> O <sub>2</sub>	1/70	3.90	80	74	575	1.68	20.0	9.97	13.6	13.3	7.2	CK
II-69 12/24/69 4%Cu(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> 1.5%Cr H <sub>2</sub> O <sub>2</sub>	1/70	3.90	80	74	575	1.68	20.0	9.88	3.6	4.0	7.3	CK
II-69 12/24/69 4%Cu(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> 1.5%Cr H <sub>2</sub> O <sub>2</sub>	1/70	3.90	80	74	575	1.68	20.0	10.20	3.5	3.9	6.9	CK
II-76 3/9/70 8%Cu(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> NH <sub>3</sub> H <sub>2</sub> O <sub>2</sub>	3/70	3.96	80	75	575	1.68	20.0	10.65	27.6	27.3	7.2	CK
II-76 3/9/70 8%Cu(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> NH <sub>3</sub> H <sub>2</sub> O <sub>2</sub>	3/70	3.96	80	75	575	1.68	20.0	10.75	29.6	29.3	6.8	CK
Control II-75(a) 3/24/70	3/70	3.93	80	82	575	1.68	20.0	8.60	10.4	10.1	7.2	CK
II-75(a) 3/24/70	3/70	3.87	80	82	575	1.68	20.0	8.49	10.6	10.1	7.4	CK
II-75(a) 3/24/70	3/70	3.96	80	82	575	1.68	20.0	10.61	13.4	12.8	7.4	CK
II-75(a) 3/24/70	3/70	3.96	80	82	575	1.68	20.0	10.27	10.9	10.8	7.2	CK

\*Bed Area is 2.93 cm<sup>2</sup>.

APPENDIX  
EDGEWOOD ARSENAL BREAKTHROUGH TIME TESTS FOR VARIOUS IMPREGNATED CARBONS

Sample No.	Date	Inlet Conc. mg/L	Relative Humidity	Dry Bulb Temp. °C	Velocity cm/min	Volume Flow L/min	Carbon Volume cm <sup>3</sup>	Carbon Weight g	Protective Life Min	Bed Depth cm	Gas
11-77 3/26/70 4%Cu (NH <sub>4</sub> CO <sub>3</sub> 1.5%Cr H <sub>2</sub> O, NH <sub>3</sub> )	3/70	3.98	80	82	575	1.68	20.0	9.98	37.1	36.3	7.1 CK
11-77 3/26/70 4%Cu(NH <sub>4</sub> CO <sub>3</sub> 1.5%Cr H <sub>2</sub> O, NH <sub>3</sub> )	3/70	3.98	80	82	575	1.68	20.0	10.45	39.3	38.5	7.1 CK
11-78 3/25/70 4% Cu NH <sub>4</sub> CO <sub>3</sub> 3%Cr H <sub>2</sub> O	3/70	3.98	80	82	575	1.68	20.0	9.83	19.0	18.6	7.0 CK
11-78 3/25/70 4%Cu NH <sub>4</sub> CO <sub>3</sub> 3%Cr H <sub>2</sub> O	3/70	3.87	80	82	575	1.68	20.0	9.69	12.6	12.1	7.2 CK

# APPENDIX III

EDGEWOOD ARSENAL BREAKTHROUGH TIME TESTS FOR PLATINUM IMPREGNATED CARBONS  
t5% Penetration (minutes) / t95% Penetration (minutes)

Percent Pt Impregnation	Bed t °C	No. H <sub>2</sub> Purge	H <sub>2</sub> Purge 25°C	H <sub>2</sub> Purge 75°C	H <sub>2</sub> Purge 100°C	H <sub>2</sub> Purge 350°C
None	25	83/149			90/151	
	75	70/132	80/142	82/137		
	100	50/109			77/120	
0.5%	25	82/165			66/144	76/135
	75	75/136	91/129	82/134		
	100	53/106			80/124	
1.0%	25	74/142			91/152	
	75	75/127	66/155	88/151		
	100	56/112			69/142	



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13. ABSTRACT This report summarizes the accomplishments of a 13 mo program to study vapor impregnation processes as a means for producing carbons having increased protection against toxic agents. Processes were developed for the vapor impregnation of carbon with cupric oxide, chromium trioxide, aluminum chloride and platinum. Spectrographic analysis of impregnated samples indicated that impregnants were present on these carbons in the expected concentration range. BET surface area analysis proved that material deposited by vapor impregnation processes caused less loss of surface area than equal amounts of material deposited by conventional solution processes. Pore size distribution calculations revealed that vapor impregnation processes deposited material in all carbon pores, while solution processes deposit material only in pores larger than 12 Å in diameter. Copper-chromium (oxide) vapor impregnated carbons were subjected to treatments designed to produce an impregnant with CK activity similar to a solution impregnated ASC carbon. Samples were produced which had greater CK activity than an unimpregnated carbon, but less activity than an ASC carbon. Future work plans designed to optimize the vapor deposition and treatment of copper-chromium oxides, to produce carbon with several times the CK capacity of an ASC, are reviewed.		

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Copper Impregnation Chromium Impregnation Aluminum Chloride impregnation Platinum Impregnation Spectrographic Analysis Nitrogen Adsorption Isotherm Pore Size Distribution Electron Microscopic Examination Detoxification Tests HCl Tests CK Tests						

Security Classification